

## Structure determination of two-dimensional adenine crystals on graphite

J. E. Freund, M. Edelwirth, P. Kröbel, and W. M. Heckl

*Institut für Kristallographie und Mineralogie der Universität München, Theresienstrasse 41, D-80333 München, Germany*

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Two-dimensional molecular-packing structure and monolayer preparation of adenine adsorbates on the graphite (0001) surface have been studied using scanning tunneling microscopy, low-energy electron diffraction, and thermal-desorption spectroscopy. By combining real-space images and diffraction data a close-packed hydrogen-bonded network of adenine dimers is proposed, containing two dimers in a unit cell with the symmetry group  $p2gg$ . The energy-minimized molecular arrangement could be determined by force field calculations. Adenine adsorbate layers were prepared by sublimation in UHV. [S0163-1829(97)02403-X]

### I. INTRODUCTION

Organic monolayers deposited on metallic or semiconductor substrates have been the subject of a large number of high-resolution scanning tunneling microscopy (STM) studies in the past years.<sup>1</sup> For several classes of organic molecules such as, for example, liquid crystals,<sup>2</sup> phthalocyanines<sup>3</sup> or alkanes<sup>4</sup> the adsorption structure could be determined based on STM images. A necessary requirement in these studies was the possibility of attributing specific parts of the molecules unambiguously to the observed STM contrast. This is mainly feasible with molecules of a characteristic shape. For a great number of organic molecules, however, the connection between topography of the STM image and the molecular orientation and arrangement is not obvious. Therefore STM on organic molecules should be used in combination with other surface science techniques which are well established for the investigation of atomic adsorbates or small inorganic molecules. Electron diffraction seems to be particularly suited for this, because it provides adsorbate-specific geometrical parameters in the reciprocal space. Reports on the combination of these methods for organic adsorbates are scarce. Examples include the structure determination of perylene-3,4,9,10-tetra-carboxylic-dianhydrid (PTCDA) on graphite<sup>5,6</sup> and thiophenes on Ag(111).<sup>7,8</sup>

Biological functions of molecules are strongly related to their structural features. The complementary base pairing through hydrogen bonds in DNA which assures the replication of the hereditary information is an important property which can be studied in two-dimensional crystals of homopurines. STM in ambient air has previously been used to study the self-assembly of some purine and pyrimidine bases following thermal evaporation of their aqueous solutions on graphite and on molybdenite.<sup>9,10</sup> The spontaneous condensation and ordering of these molecules deposited under electrochemical control in solution<sup>11</sup> onto graphite or crystalline gold surfaces<sup>12</sup> has been investigated by (electrochemical) STM and atomic force microscopy (AFM). For adenine on graphite different models have been proposed for the molecular packing structure.<sup>9,11,12,17</sup> The differences might be explained by either the formation of different crystal structures according to the preparation conditions, or by simply being due to the difficulties in STM image interpretation.

Therefore the aim of this work has been to derive a clear cut structural model for adenine on graphite by combining

STM and low-energy electron-diffraction (LEED) data. The geometric structure determination is a presumption of the advance in understanding the molecular image contrast in STM. This is necessary especially in the case when the spatial distribution of electron density of states does not coincide in a simple way with the geometrical packing structure, as found in many cases with a graphite substrate.

### II. EXPERIMENT

Adenine films were prepared by molecular-beam deposition. For sublimation the adenine powder was heated to 200 °C, and the substrate was kept at 60 °C. The vacuum pressure during the sublimation process was below  $5 \times 10^{-10}$  mbar. Although a direct deposition control was not available, the optimum preparation parameters together with the adsorption energy have been determined by thermal-desorption spectroscopy.<sup>13</sup> Mass spectra showed that the adenine molecules were intact after sublimation and adsorption.

Except for the STM measurements, all experiments were carried out in UHV. Natural graphite was used as substrate for LEED investigations. Prior to the UHV experiments the crystallinity was checked by Laue x-ray scattering. Since graphite is a very inert material, surface preparation of the freshly cleaved graphite has been confined to tempering at 500 °C for 48 h.

The LEED experiments were performed at room temperature with reverse view electron optics. Adsorbate-induced LEED patterns have been measured in an energy range between 10 and 40 eV. No degradation of the pattern could be observed at electron beam intensities of several 100 nA for about 1 h.

The STM measurements were performed with a home built instrument. All images were obtained with electrochemically etched W tips. Image calibration including the removal of distortions was done by comparing STM images of molecular adsorbates with the underlying substrate. The STM image shown below was acquired in the constant current mode with the typical tunneling current of about 90 pA and 1.0 V (tip negative).

### III. RESULTS AND DISCUSSION

#### A. LEED

The LEED pattern of a monolayer adenine film on graphite with an electron beam energy of 14.5 eV is shown in Fig.

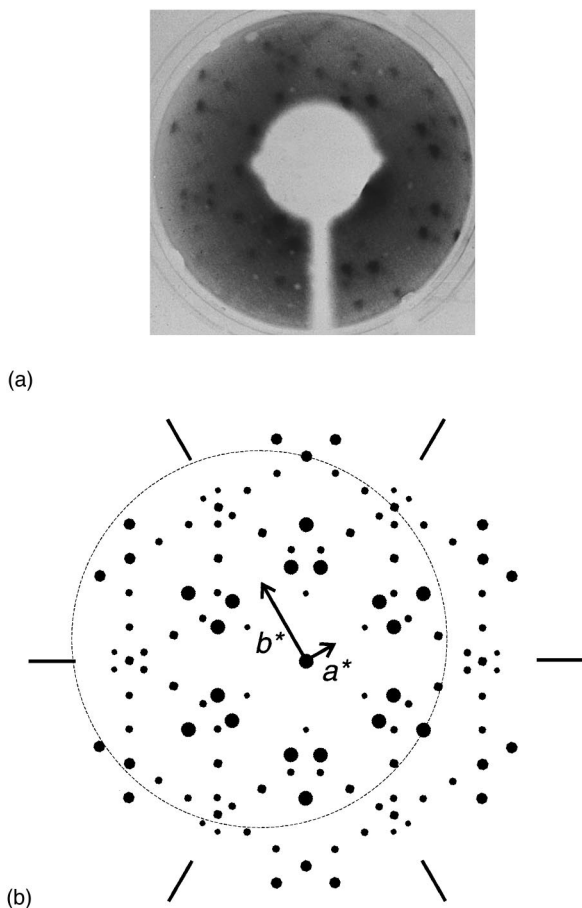


FIG. 1. (a) LEED pattern of an adenine monolayer with  $E = 14.5$  eV at nearly normal incidence. (b) Kinematic calculation of the LEED pattern with the structure proposed in Fig. 4. The peak diameters are scaled logarithmically. The three symmetry-equivalent domain orientations are taken into account. The directions of the first-order graphite reflexes are marked by radial lines, and the reciprocal unit cell is indicated for one domain. The dashed ring surrounds the visible area of the pattern in (a).

1(a). The absolute size and the shape of the unit cell are determined from this pattern. Together with the LEED reflexes from graphite, which can be observed at higher beam energies, the relative unit cell of the molecular lattice and its mutual orientation can be expressed in unit vectors of the underlying graphite.

We first note that the LEED image shows singular spots arranged in a hexagonal symmetry. Therefore it can be concluded that the adsorbate grows in an epitaxial way with a registry of the overlayer structure to the graphite. From STM results we find that the typical size of an adenine domain is in the range of several hundred to few thousand Å. Because the electron beam ( $\sim 1$  mm in diameter) covers a great number of domains all possible growth orientations of the adsorbate are contained in the LEED pattern.

For the unit cell a rectangular shape ( $90 \pm 1^\circ$ ) with vectors  $\mathbf{a} = 22 \pm 1$  Å and  $\mathbf{b} = 8.5 \pm 0.5$  Å is obtained. Vector  $\mathbf{a}$  points in the direction of the graphite lattice vector  $\mathbf{g}_1$ . Assuming a commensurate adsorbate superstructure the relative unit cell can be derived as  $\begin{pmatrix} 9 & 0 \\ -2 & 4 \end{pmatrix} \begin{pmatrix} g_1 \\ g_2 \end{pmatrix}$ , with the graphite lattice vec-

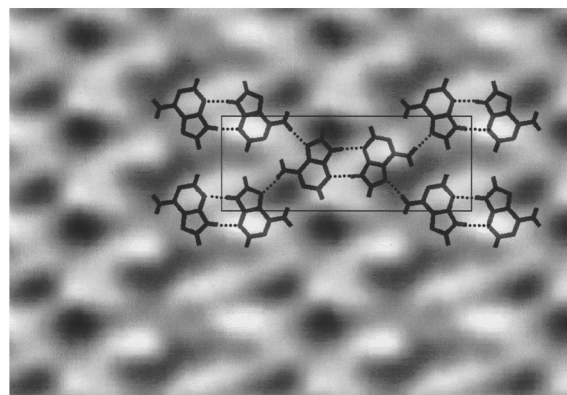


FIG. 2. STM image of an epitaxially grown monolayer of adenine on graphite (0001) with molecule positions indicated (size of the imaged area:  $48 \times 32$  Å<sup>2</sup>;  $U = 1.0$  V,  $I = 90$  pA, constant current mode).

tors  $\mathbf{g}_1$  and  $\mathbf{g}_2$  and  $|\mathbf{g}_1| = |\mathbf{g}_2| = 2.46$  Å (see Fig. 4). From this expression we expect the exact dimensions to be  $|\mathbf{a}| = 22.14$  Å and  $|\mathbf{b}| = 8.52$  Å. The interpretation of a commensurate structure is strongly encouraged by the brightness of the LEED reflexes as well as by the STM measurements. Figure 1(b) shows a calculation of the LEED pattern in a kinematic approximation<sup>14</sup> based on the structure model of the unit cell discussed below. For the calculation a unit cell of the adsorbate with four graphite layers underneath is used. All equivalent rotations of the molecular lattice are taken into account. The calculation yields the correct reflex positions as well as the observed extinction of the  $(0\ 2k+1)$  and the  $(2h+1\ 0)$  reflections. The relative intensities are qualitatively reproduced. From the extinctions two orthogonal glide symmetry planes parallel to the  $\mathbf{a}$  and  $\mathbf{b}$  axes can be derived.<sup>15</sup>

The symmetry elements severely reduce the possible relative orientations of the molecules in the unit cell. In fact it is not possible to construct a unit cell under these restrictions with single adenine molecules because of the asymmetry of the molecule. Therefore as unit-cell elements we propose H-bonded adenine dimers with a twofold symmetry each. This assumption is supported by the self-association of adenine molecules under typical experimental conditions.<sup>16</sup> The detailed structure of the unit cell is discussed in Sec. III C.

## B. STM

Figure 2 shows a constant current mode STM image of a single domain region of the molecular lattice on graphite. Bright regions correspond to elevated areas and dark regions to depressions. Because the corrugation contains both geometrical features and variations of the electronic structure of the adsorbate a straightforward assignment of the compact molecules to distinct sites of the image is not possible. However, a unit cell of the molecular lattice can be determined immediately from the contrast pattern: With  $\mathbf{a} = 21.5 \pm 1$  Å and  $\mathbf{b} = 8.5 \pm 0.5$  Å and the angle between  $\mathbf{a}$  and  $\mathbf{b}$ ,  $\gamma = 90 \pm 1^\circ$ , the unit cell agrees within the experimental accuracy with the LEED measurement. The same holds for the orientation of the molecular lattice to the underlying graphite. A comparison of the orientations was possible by imaging the bare graphite at a reduced tunneling resistance which, how-

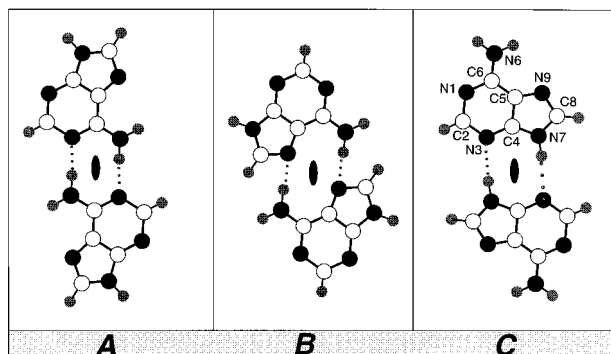


FIG. 3. Three different possibilities of hydrogen-bonded adenine dimers with a twofold symmetry center.

ever, destroyed the adsorbate film. Contrast modulations with periodicities longer than the unit cell which are typical of coincident adsorbate growth could not be detected in the STM images.

It is remarkable that the same unit-cell vectors were found for different experiments under various conditions. Besides the vacuum sublimated films, we found identical results with adsorbates that were dried from solution on a hot plate in ambient air. Also congruent herewith are the earlier results by Heckl<sup>17</sup> after a recently performed recalibration of the STM data. The same cell vectors were also reported by Tao and Shi,<sup>11</sup> imaged in NaCl solution by electrochemical AFM. However, a different molecular arrangement was proposed because glide symmetries could not be determined. The STM data shown by Allen *et al.*<sup>9</sup> can also be interpreted in agreement with the above lattice if a different unit cell is chosen. These results with adsorbate films grown under different preparation conditions strongly indicate that adenine on graphite forms one stable phase by the specific lateral hydrogen bonding and by a defined registry with the graphite substrate.

### C. Model building and verification

More complex than the shape of the unit cell is the determination of its packing structure. Force-field calculations together with symmetry arguments and chemical information were applied to exclude competing structure models.

A structure model was built starting with two symmetrically bonded adenine dimers. The number of four adenine molecules has been chosen because of the area of about  $50 \text{ \AA}^2$  per molecule in the molecular plane. Only one dimer can be chosen arbitrarily; the second dimer in the unit cell is then determined by the glide symmetries. There are three possible ways of self-associating adenine with two hydrogen bonds and a twofold symmetry center (see Fig. 3). For each configuration a model was constructed with the first dimer lying flat on the origin of the unit cell. Thus the second dimer is centered on  $\mathbf{a}/2 + \mathbf{b}/2$ . The remaining Euler angle in the adsorption plane was chosen in a way that the overlap with other dimers was minimized. These “coarse” models were used as starting configurations for force-field calculations. In the calculations the energy of the adsorbate structure was minimized by variation of the exact molecular positions.<sup>18</sup> Periodic boundary conditions were applied. For the minimization the unit-cell dimensions in terms of the graphite lattice

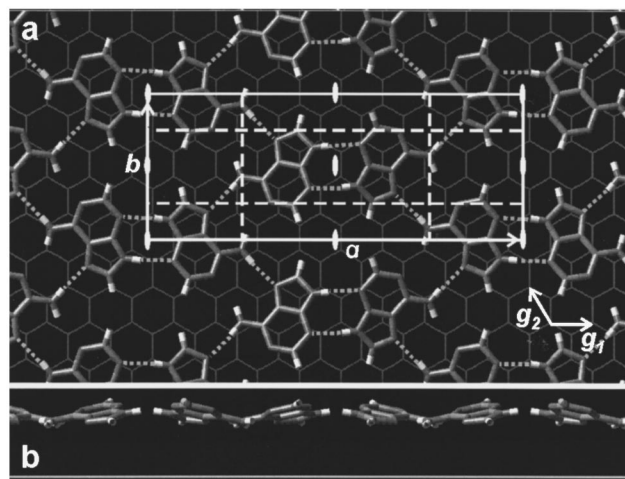


FIG. 4. Model of the unit cell. (a) View perpendicular to the graphite layers. The rectangular cell has its vector  $\mathbf{a}$  parallel to  $\mathbf{g}_1$  with  $a=22.1 \text{ \AA}$  and  $b=8.5 \text{ \AA}$ . It contains two adenine dimers which comply with the orthogonal set of glide symmetry planes parallel to  $\mathbf{a}$  and  $\mathbf{b}$ . (b) View parallel to the surface. The first graphite layer is indicated by the bottom line.

vectors were kept fixed at the experimentally determined values. The graphite substrate was represented by a four-layer slab. Each adenine molecule was allowed to move independently in all six degrees of freedom. The termination criterion for the iterative process was a derivative of the energy surface smaller than  $10^{-5} \text{ kcal}/(\text{mol \AA})$ . A detailed description of the calculations will be published elsewhere.

The structure model shown in Fig. 4 and the molecules pasted into the STM image (Fig. 2) show the final arrangement after the minimization with type-C associated dimers. Apart from some directional and bond length fine tuning the main difference from the “coarse” starting geometry is that the molecules are tilted [see Fig. 4(b)] similarly to the propeller twist observed in cocrystals of nucleosides. This occurs for all molecules in the same way, and retains the glide symmetries. As indicated in Fig. 5, the center of mass of each molecule has a vertical distance of  $3.57 \text{ \AA}$  from the graphite plane. Two angles  $\alpha$  and  $\beta$  are defined between the graphite normal, the center of mass, and the atoms  $C_2$  and  $C_8$ , respectively. For the inclination  $\alpha=102.6^\circ$  and  $\beta=83.6^\circ$  is obtained.

Based on the following reasons we propose the model shown in Fig. 4 for the adsorbate structure: (1) Although no

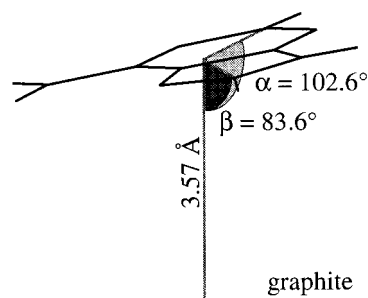


FIG. 5. Schematic presentation of the tilted molecule seen parallel to the graphite layer. For the angle definition, see text.

symmetry restrictions are made in the calculation, the final arrangement obeys the two orthogonal glide symmetry planes observed in the LEED measurement. The final configurations of both other models strongly break this symmetry. (2) A pronounced network of hydrogen bonds is reached. Each adenine molecule is fixed in a network of four hydrogen bonds which all have the length  $2.94 \pm 0.02$  Å. This is well within the range of  $\text{NH} \dots \text{N}$  bond lengths which can be found between 2.75 and 3.15 Å.<sup>16</sup> Additionally the infinite chain of hydrogen bonds  $\text{N}_6\text{H} \dots \text{N}_9$  enhances the stability because of  $\pi$  cooperativity.<sup>19</sup> (3) For this configuration the force-field calculation reaches the lowest total energy, and it is the only model which satisfies the termination criterion. (4) The kinematic simulation of the LEED pattern yields a qualitative correspondence with the observed intensities with this model only, and it diverges significantly for the other proposed structures. (5) The observed STM contrast can be explained in terms of geometrical effects. The maximum height difference between atoms in the molecule is 1.3 Å, a variation which would change the tunneling current by about one order in magnitude. The eight bright spots in the STM image can be attributed to the geometrically most protruding sites of the tilted molecules.

#### IV. CONCLUSIONS

Using the complementary techniques STM and LEED, monolayer adenine adsorbates on graphite were analyzed.

These different methods yielded congruent results regarding the form and orientation of the molecular superlattice. A detailed crystallographic structure is proposed based on molecular resolution STM images and LEED measurements which convey information about orthogonal glide symmetries. Symmetrical constraints can be satisfied by hydrogen-bonded adenine dimers as basic elements. Out of three competing structure models the correct arrangement of the molecular crystal could be determined by a force-field calculation. The calculation yields a small tilt of the molecules, and preserves the symmetry constraints. The molecular structure is commensurate with the graphite substrate, and forms a hydrogen-bonded network with four bonds per molecule. The contrast in the STM image can be interpreted as dominated by geometrical height variations of the tilted molecules.

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